

# Roton-Rotation Coupling of Acetylene in $^4\text{He}$

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Rotational absorption spectra of acetylene in superfluid  $^4\text{He}$  are calculated using a combined correlated basis function-diffusion Monte Carlo method (CBF/DMC) as well as a numerically exact path integral correlation function approach (PICF). Both approaches predict anomalously large distortion constants in addition to reduced rotational constants, and the higher rotational excitations are seen to be accompanied by an additional peak and absorption band. The CBF analysis shows that these phenomena are due to strong coupling of the higher rotational states with the roton and maxon excitations of  $^4\text{He}$ , and the associated divergence of the helium density of states in this region.

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Helium nanodroplets have become a useful matrix for isolation spectroscopy [1]. Unlike in classical liquids, the spectra of embedded molecules may be rotationally resolved in the superfluid environment of  $^4\text{He}$ , which has led to numerous investigations of rotational constants of molecules in  $^4\text{He}$  droplets (see table 1 in Ref. [2]). For all but the lightest rotors, a significant reduction of the rotational constants with respect to their gas phase values has been found, with identical symmetry, which has been explained by the adiabatic following of a molecular-interaction induced non-superfluid fraction of the solvation shell.[3] In contrast, the lightest molecules exhibit relatively small reduction of their rotational constants in  $^4\text{He}$  droplets [2]. Calculations have shown that the assumption of adiabatic following breaks down for light molecules [4] and that instead of coupling to localized helium solvation density, there is appreciable coupling to delocalized collective helium modes [5].

Acetylene ( $\text{HCCH}$ ) is one such light molecule, whose ro-vibrational spectrum has been obtained by infra-red spectroscopy in  $^4\text{He}$  droplets [6]. The effective rotational constant  $B_{\text{eff}}$  was found to be reduced to 88% of its gas phase value ( $1.1766 \text{ cm}^{-1}$ ) and a very large effective distortion constant  $D_{\text{eff}}$  was measured, showing a relative enhancement  $D_{\text{eff}}/B$  an order of magnitude larger than that seen for heavier molecules such as  $\text{OCS}$ ,  $\text{SF}_6$  and  $(\text{HCN})_2$ . It was speculated that the excessive broadening of the IR spectral lines might indicate coupling to excitations of the helium, but in the absence of theoretical understanding of such a coupling no conclusions could be drawn. The calculations of the rotational absorption spectra of  $\text{HCCH}$  presented here show how coupling between the molecular rotation and the roton excitations of  $^4\text{He}$  results in an anomalously large distortion constant as well as a reduced rotational constant, with predicted values in good agreement with experimental measurements. They also reveal that the higher rotational excitations display a secondary peak as well as a weak maxon-roton band between them that both result from this coupling. We discuss how these additional spectral features might be observed, in order to stimulate experiments to measure this unique signature of rotation-roton coupling.

We present two independent calculations. The first calculation is a combination of correlated basis function (CBF) theory and diffusion Monte Carlo (DMC) methodology that derives zero temperature excitation energies from linear response theory for correlated wave functions [7] and then evaluates these with numerically exact DMC calculations for the required input ground state properties [5]. The rotational excitations are described in this CBF/DMC approach within an analytic approximation that reveals the microscopic origins of the rotational excitations and associated spectral absorption features. For the second calculation we use path integral Monte Carlo methods [8, 9] (at temperature  $T = 0.625 \text{ K}$ ) to evaluate the imaginary-time orientational correlation functions  $F_J(t) = (1/Z) \sum_m \text{Tr}\{Y_{Jm}^+(\Omega(t))Y_{Jm}(\Omega(0))e^{-H/kT}\}$  ( $\Omega$  is the molecular orientation), sampled from the full molecule-helium Hamiltonian  $H$  that includes molecular rotation and all translational degrees of freedom as well as the permutation exchange symmetry of helium [10]. The inverse Laplace transform (made with the maximum entropy method [11]) of  $F_J(t)$  is proportional to the rotational absorption spectrum for dipole ( $J = 1$ ), quadrupole ( $J = 2$ ), and higher order transitions. The PICF calculation provides a quantum simulation free from systematic approximation which is important for verification of the novel spectroscopic features predicted by the CBF/DMC calculations.

In Ref. [5], we formulated the CBF/DMC approach for molecular excitations in  $^4\text{He}$  and showed how CBF theory is able to describe the effect of coupling of collective excitations of the  $^4\text{He}$  environment to the rotational dynamics of a molecule. This coupling was seen to renormalize the rotational energy  $\hbar\omega_J$  corresponding to total angular quantum number  $J$  for a linear molecule with bare mass  $M$  and gas phase rotational constant  $B$  by an energy-dependent self energy  $\Sigma_J(\omega_J)$  [12],

$$\hbar\omega_J = BJ(J+1) + \Sigma_J(\omega_J) \quad (1)$$

which is a functional of several ground state quantities [5]. The Legendre coefficients  $g_{\ell'}(r)$ ,  $\ell' > 0$ , of the pair distribution function between  $\text{HCCH}$  and  $^4\text{He}$

are obtained from a DMC simulation of HCCH and 256  $^4\text{He}$  atoms (periodic boundary conditions), employing a trial wave function of the form used in Ref. [5] (parameters  $c = 7.724 \text{ \AA}$  and  $b = 2.670 \text{ \AA}$ ), interaction potentials from Refs. [14, 15], and implementing descendent weighting [16]. Odd components of  $g_{\ell'}(r)$  vanish for HCCH and the zero component  $g_{\ell'=0}(r)$  does not contribute to  $\Sigma_J(\omega)$ , so that the  $\ell' = 2$  coefficient is the dominant contribution to  $\Sigma_J(\omega)$ . From angular momentum conservation [5], one can then show that for HCCH the dominant effect of the superfluid  $^4\text{He}$  environment on the molecular rotational excitations  $J$  is the coupling of molecular rotational states that differ by  $|J - \ell| = 2$ .

In general, the self energy is complex, leading to finite life-times and decay of rotational excitations into other modes. When the momentum  $p$  is such that the input energy  $\hbar\omega$  equals the sum of three excitation energies  $B\ell(\ell+1)$  (molecular rotation),  $\epsilon(p)$  (phonon-roton excitation), and  $\hbar^2 p^2/2M$  (kinetic energy of the recoiling HCCH), these states can be excited by decay of the rotational excitation  $\hbar\omega = \hbar\omega_J$ .

Eq. (1) needs to be solved self-consistently for  $\omega_J$  since the self energy  $\Sigma_J(\omega_J)$  is itself a function of  $\omega_J$ . When the imaginary part of  $\Sigma_J$  is small, the real part of the solutions are seen to correspond to the positions of well-defined peaks in the dipole ( $J = 1$ ), quadrupole ( $J = 2$ ), ... absorption spectra of the molecule from its ground state. These spectra, normalized to unity, are given by

$$\begin{aligned} S_J(\omega) &= \frac{1}{\pi} \Im m[BJ(J+1) + \Sigma_J(\omega) - \hbar\omega]^{-1} \\ &= \frac{\Im m \Sigma_J(\omega)/\pi}{(\gamma_J(\omega) - \hbar\omega)^2 + (\Im m \Sigma_J(\omega))^2}, \end{aligned} \quad (2)$$

where we have defined  $\gamma_J(\omega) = BJ(J+1) + \Re e \Sigma_J(\omega)$ . The imaginary part of the self energy,  $\Im m \Sigma_J$ , gives the homogeneous width of the Lorentzian line associated with decay of the excitation of life-time  $\hbar/\Im m \Sigma_J(\omega_J)$  into the lower energy modes of the molecule (rotation and translation) accompanied by emission of a  $^4\text{He}$  excitation. In the opposite limit when the imaginary part of  $\Sigma_J(\omega)$  is large, eq. (2) shows that the absorption  $S_J(\omega)$  can become large regardless of whether or not  $\omega$  is a solution of eq. (1). In this case we find a broad band which cannot be uniquely associated with a single molecular rotation mode, but instead is due either to a simultaneous excitation of both the molecular rotation and  $^4\text{He}$  modes, or of only  $^4\text{He}$  modes (see below).

Fig. 1 shows the ground state absorption spectra of HCCH for  $J = 1, 2, 3$  calculated by CBF/DMC, eq. (2). The rotational excitations obtained from PICF are also shown, as broad solid lines with height proportional to their spectral weight. Lineshapes and broad spectral features cannot be obtained with the correlation function spectral inversion approach, but the positions and relative strength of discrete peaks are very reliable [17]. The

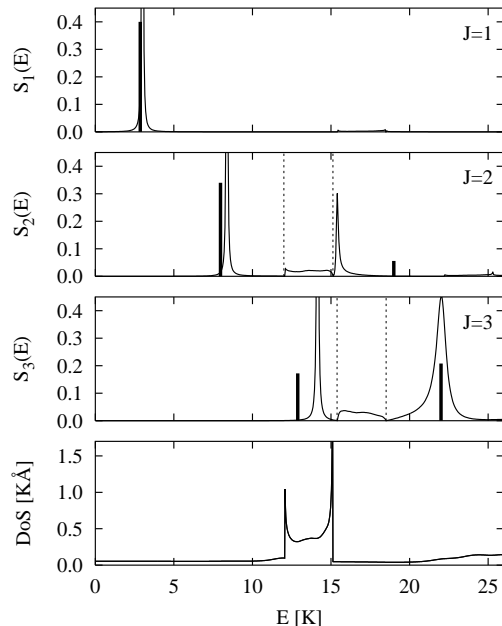


FIG. 1: CBF/DMC absorption spectra  $S_J(\omega)$ ,  $J = 1, 2, 3$ , for HCCH in bulk  $^4\text{He}$  (thin solid lines) and PICF rotational excitations (broad solid lines, height proportional to the spectral weight) for HCCH in a cluster of 64  $^4\text{He}$ . The CBF/DMC spectra have been broadened by 10 mK. The bottom panel shows the density of states  $\epsilon'(p) + \hbar^2 p^2/2M$ . The vertical dotted lines in the  $J = 2$  and  $J = 3$  panels indicate the edges of the roton-maxon bands coupling these states to  $\ell = 0$  and  $\ell = 1$  states, respectively.

CBF/DMC spectra have sharp Lorentzian peaks associated with excitations of finite life-time, as well as broad features between these peaks. The peaks are in good qualitative agreement with the PICF excitations, which are made for HCCH in a cluster of 64  $^4\text{He}$  atoms (approximately two solvation layers). This implies that the relevant  $^4\text{He}$  collective excitations are already well developed at this cluster size and that the rotational coupling to these modes is not sensitive to temperature variation below  $T \sim 0.6 \text{ K}$ .

We analyze first the sharp peak structures. The locations  $\hbar\omega'$  of peaks in the CBF/DMC spectrum  $S_J(\omega)$  are found by solving the equation  $\gamma_J(\omega) - \hbar\omega = 0$  (see also eq. 2), which can have one or more solutions. Each solution  $\hbar\omega'$  can be associated with a rotational excitation of finite life-time, which can decay into a  $\ell < J$  state and an excitation of the helium environment. It is evident from Fig. 1 that while for  $J = 1$  a single peak is obtained, the CBF/DMC absorption spectra  $S_J(\omega)$  for  $J = 2$  and  $J = 3$  have *two* peaks each, in contrast to the expected pattern of excitations for a linear rotor which has only a single excitation at energy  $BJ(J+1)$  for a given  $J$ . This surprising double peak feature is also found for the rotational excitations calculated with the numerically exact PICF method. The latter do not rely on any analytic

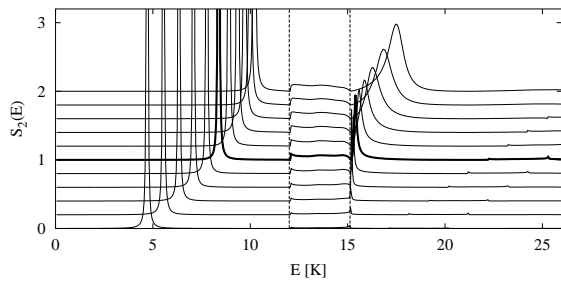


FIG. 2: The absorption spectrum  $S_J(\omega)$ , for the  $J = 0 \rightarrow 2$  transition of HCCH in  $^4\text{He}$ , where we have varied the gas phase rotational constant  $B$  between  $0.5 \times B$  (bottom curve) and  $1.5 \times B$  (top curve), in steps of  $0.1 \times B$ .

approximations and thus provide additional verification of the correctness of the splitting seen in the CBF/DMC spectra. We therefore are led to conclude that unlike heavier rotors such as OCS, the pure rotational spectrum of HCCH in  $^4\text{He}$  for excitations higher than  $J = 1$  does not conform with the simple pattern predicted for an effective linear rotor.

Inspection of the CBF equations allows us to determine that the reason for the occurrence of two peaks for absorptions to  $J = 2$  and  $J = 3$  is the non-monotonic behavior of the collective excitation spectrum in  $^4\text{He}$ . The divergent density of states (see bottom panel of Fig. 1) at both the roton minimum (wave number  $p_r$ ) and the maxon maximum (wave number  $p_m$ ) of the helium excitation spectrum [13] results in divergences in the self energy  $\Sigma_J(\omega)$  at  $\omega = B\ell(\ell + 1) + \varepsilon(p) + \hbar^2 p^2 / 2M$  for  $p = p_r, p_m$  and  $\ell = 0, 1, 2, \dots$ . These divergences can split spectral peaks that are close to the roton and maxon into two, shifting the “primary” peak below the roton minimum and moving the “secondary” peak above the maxon maximum [5]. The dipole spectrum,  $J = 1$ , has only a single peak, because the  $J = 1$  excitation energy is much lower than the roton energy and consequently does not couple so effectively to the collective modes. Consequently the secondary  $J = 1$  absorption peak has negligible weight and is not observed. For  $J = 2$ , the weight of the secondary peak is small but non-negligible, while for  $J = 3$  more than half of the spectral weight is actually carried by the secondary peak, see Table I.

In order to further understand the coupling between rotations and rotons that is implied by this splitting, we have calculated the CBF/DMC spectrum as a function of the molecular gas phase rotational constant  $B$ . This allows the molecular rotational energy to be tuned across the roton/maxon energy regime, and the coupling between molecule and helium to be modulated as a result. Fig. 2 shows the quadrupole spectrum  $S_J(\omega)$ ,  $J = 2$ , as  $B$  is artificially varied between  $0.5 \times B$  and  $1.5 \times B$  in eq. (2) and in the expression for the self energy. For simplicity we use the same molecule-helium pair distribution

| $J$ | CBF              |      | PICF             |      | Exp. |
|-----|------------------|------|------------------|------|------|
|     | E [cm $^{-1}$ ]  | $w$  | E [cm $^{-1}$ ]  | $w$  |      |
| 1   | $2.08 \pm 0.04$  | 0.98 | $1.99 \pm 0.10$  | 1.00 | 2.01 |
| 2   | $5.82 \pm 0.24$  | 0.82 | $5.54 \pm 0.10$  | 0.85 | 5.55 |
| 2'  | $10.70 \pm 1.31$ | 0.08 | $13.20 \pm 0.90$ | 0.14 | —    |
| 3   | $9.82 \pm 0.69$  | 0.33 | $8.95 \pm 0.41$  | 0.43 | —    |
| 3'  | $15.28 \pm 0.70$ | 0.49 | $15.28 \pm 0.53$ | 0.52 | —    |

TABLE I: Rotational excitation energies of HCCH in  $^4\text{He}$  calculated with CBF (bulk  $^4\text{He}$ ) and PICF ( $^4\text{He}_{64}$ ), for  $J = 1, 2, 3$ , compared with experimental values extracted from IR spectra [6].  $J'$  denotes the secondary peaks and  $w$  the respective spectral weights.

function for all  $B$  values in this comparison. When the gas phase value of  $B$  is sufficiently small that the  $J = 2$  excitation does not couple to the roton excitations it is evident that  $S_2(\omega)$  now shows only a single peak, just like  $S_1(\omega)$  in Fig. 1. On increasing  $B$  to its actual gas phase value,  $1.1766\text{cm}^{-1}$ , the secondary peak is seen to emerge and simultaneously a weak roton-maxon band starts to grow in between the two peaks. On increasing  $B$  beyond the HCCH value, the secondary peak continues to grow until it eventually accounts for the entire spectral weight and the primary peak vanishes.

Between these two peaks in the  $J = 2, 3$  spectra, there are no sharp rotational peaks because excitations here would decay instantaneously due to the high density of states between the roton and maxon excitations of  $^4\text{He}$ . The resulting large imaginary part of  $\Sigma_J(\omega)$  leads to a broad roton-maxon band in the spectrum. (Unfortunately such broad features cannot be retrieved from analytic continuation of the PICF to real frequencies.) Although these roton-maxon bands appear small in Fig. 1, they do possess non-negligible weights of 0.06 and 0.08 in the  $J = 2$  and  $J = 3$  spectra, respectively. The roton-maxon band for  $J = 3$  is shifted in energy by  $2B$  with respect to the corresponding band for  $J = 2$ , because for  $J = 2$  the molecular rotation is coupled to a pure excitation of the helium environment with the molecule in its rotational ground state  $\ell = 0$ , while for  $J = 3$ , the rotation is coupled to an  $\ell = 1$  molecular state. In both cases  $J - \ell = 2$ , which corresponds to the strongest contribution to the self energy  $\Sigma_J(\omega)$ , as noted above.

We now consider how these CBF and PICF results may be observed experimentally. Our ground state spectra correspond to dipole, quadrupole, etc. rotational absorption from the  $J = 0$  ground state, while in Ref. [6] rotational transitions  $J = 0 \leftrightarrow 1$  and  $J = 1 \rightarrow 2$  were observed (accompanied by excitation of the C-H vibrational stretches). Table I compares the CBF and PICF rotational excitations with the experimental values extracted in [6]. The two excitations  $J = 1$  and  $J = 2$  that were accessed by the spectroscopic measurements are seen to be in excellent agreement with the theoret-

| HCCH             | CBF    | PICF   | Exp.[6] | gas phase[6]          |
|------------------|--------|--------|---------|-----------------------|
| $B_{\text{eff}}$ | 1.075  | 1.031  | 1.042   | 1.172                 |
| $D_{\text{eff}}$ | 0.0175 | 0.0179 | 0.0195  | $1.62 \times 10^{-6}$ |

TABLE II: Rotation constant  $B_{\text{eff}}$  and distortion constant  $D_{\text{eff}}$  of HCCH in  $^4\text{He}$ . The CBF and PICF results are compared with the fit made to  $J = 0 \rightarrow 1, J = 1 \rightarrow 2$  rovibrational fine structure transitions in IR spectra [6]. (Units in  $\text{cm}^{-1}$ )

ical values for  $J = 1$  and for the primary peak of the  $J = 2$  spectrum. (The CBF self energy and accuracy of results can be further systematically improved [5].) Table II compares the spectroscopic constants  $B_{\text{eff}}$  and  $D_{\text{eff}}$  obtained by fitting these two excitations to the non-rigid linear rotor spectrum  $B_{\text{eff}}J(J+1) - D_{\text{eff}}(J(J+1))^2$ . The distortion constant relative to  $B$ ,  $D_{\text{eff}}/B$ , is very large compared to that for heavier molecules [2, 6]. Our calculations show that this anomalously large distortion constant results from the strong coupling of the  $J = 2$  excitation with the helium roton and maxon excitations. Fig. 2 shows that the spectral shift to lower frequencies that is responsible for  $D_{\text{eff}}$  is greater for lighter molecules, reflecting an increased coupling as the molecular excitation become more resonant with these helium modes that derives primarily from their high density of states. In Ref. [5] we demonstrated that this deviation from a linear rotor spectrum is much smaller when the molecule couples to a simple linear (phonon) excitation spectrum.

In this CBF calculation the homogeneous linewidth of the absorption spectra in Figs. 1 and 2,  $\Im m \Sigma_J(\omega)$ , results from rotational relaxation only. For  $J = 1$ , the rotational linewidth vanishes due to the symmetry of the HCCH- $^4\text{He}$  potential (see eq. (4.4) in Ref. [5]). For  $J = 2$ , it is finite but still smaller than the experimental IR linewidth, which is believed to also have contributions from vibrational relaxation as well as inhomogeneous broadening due to finite size effects [6]. Vibrational relaxation may lead to a reduced life-time of the secondary transition such that it is too short to be observed. Multi-phonon excitations, which become prevalent in  $^4\text{He}$  for excitation energies around 20 K and higher, and are not incorporated in the present CBF analysis, may also broaden the theoretical peaks. For HCCH the secondary peak for  $J = 2$  is predicted to lie outside the range accessed in Ref. [6] and a preliminary search for this at higher IR energies has not been successful [18], possibly for the above reasons. Another complication for comparison with the IR spectra is that the  $J = 2$  state is accessed by the dipole transition  $J = 1 \rightarrow 2$ , while the CBF calculation yields the quadrupole transition  $J = 0 \rightarrow 2$ , with different transition matrix elements for the HCCH- $^4\text{He}$  coupling. Measurement of the rotational Raman spectrum may allow a direct access to the  $J = 0 \rightarrow 2$  transition.

In summary, calculations of the rotational absorption

spectra corresponding to dipole, quadrupole, etc. transitions of HCCH from its rotational ground state in bulk  $^4\text{He}$ ,  $0 \rightarrow J$ , using the CBF/DMC and PICF approaches yield an anomalously large distortion constant  $D_{\text{eff}}$  that is seen to result from a strong coupling of the higher molecular rotation states to the roton excitation of helium. The CBF/DMC spectra for  $J = 2$  and  $J = 3$  show secondary peaks at higher energies, which are confirmed by the numerically exact PICF results, as well as weak roton-maxon bands between the two peaks. We expect that these unique signatures of coupling between roton modes of helium and rotational modes of embedded molecules will be found in Raman spectra, as well as possibly in microwave and IR spectra for other light molecules.

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